PROCEEDINGS

# TECHNOLOGY TRANSFER CONFERENCE

NOVEMBER 30 - DECEMBER 1, 1987

ROYAL YORK HOTEL

## PART D

## ANALYTICAL METHODS

Organized through the

RESEARCH ADVISORY COMMITTEE

Sponsored by

ENVIRONMENT ONTARIO

Ontario, Canada

# DIOXINS AND FURANS IN TOXIC PRECIPITATION SAMPLES

C. Tashiro and R.E. Clement
Laboratory Services Branch
Ontario Ministry of Environment
P.O. Box 213, Rexdale, Ontario
Canada M9W 5L1

M. Lusis, D. Orr and N. Reid
Air Resources Branch
Ontario Ministry of Environment
880 Bay Street, Toronto, Ontario
Canada

A wide range of organic compounds have been found to exist in locations far removed from their probable sources(1). It is assumed that long range atmospheric transport and subsequent deposition via preciptiation is the mechanism responsible for the environmental spread of these compounds. This mechanism could account for the low background levels of a variety of organic compounds found in isolated locations.

Low level chlorinated dibenzo-p-dioxins (CDD's) and chlorinated dibenzofurans (CDF'S) have been found in samples taken from remote areas(2). The long range transport of CDD's and CDF's and their subsequent deposition via atmospheric precipitation has been studied at the Ontario Ministry of the Environment.

The sample collection site chosen was Dorset, Ontario (southwest of Algonquin Provincial Park). Two sample collection methods were used in this study. The first method involved the use of a custom-designed heated sampler for the direct collection of precipitation samples into pre-cleaned five gallon jugs. In the second method, an XAD-2 cartridge was used in the same sampler and the precipitation was allowed to percolate through the XAD-2 resin into a

collection jug (See Figure 1). The sampler opened only during precipitation events (rain and snow). The precipitation was collected over a four week period. The samples were then transported to the Rexdale Laboratory, solvent extracted, subjected to the Dow column cleanup method and analyzed by GC/MS for the presence of the full range of dioxin and furan congeners. To determine if any losses occurred during the handling and collection periods, the sample bottles or cartridges were spiked using $^{13}$C-labelled congeners prior to collection. The samples were also spiked prior to extraction with a different set of $^{13}$C-isomers to allow the determination of percentage recoveries of the CDD/CDF through the analytical processing.

Sample collection was carried out in Dorset over an eight month period. In the initial stages, direct collection of rainwater into five gallon jugs was the only sample collection method used. Later, direct collection and XAD collection methods were used in parallel. The water that percolated through the XAD was collected in a jug and also analyzed for spike and/or native CDD/CDF breakthrough from the cartridge. A spiked field blank sample was always used to determine losses that may have occurred during handling and storage. In the sets of samples analyzed, no 4CDD or 4CDF (the most toxic congeners) were found at limits of detection of 4 to 30 parts per quadrillion (ppq). Positive 8CDD was found in three monthly samples in the 60-1000 ppq range (Nov/Dec'86, March/April'87 and July/Aug'87). Lower levels of 7CDD, 7CDF and 8CDF were detected in the Nov/Dec'86 samples and a very low level of 6CDF was found in the March/April'87 sample. Field spike recoveries ranged from 10-110% and lab spikes (spiked prior to extraction) ranged from 35 to 130%. Corrections were made for lab spike recovery levels. Not enough data has been collected to see whether there are any seasonal affects.



A wall loss study was also initiated due to the 1-2 month delay between the initiation of field sampling and sample extraction. Triplicate four litre water samples were spiked with $^{13}$C-4CDD and $^{13}$C-8CDD at both a low and high spike level. The samples were spiked again just prior to extraction with $^{13}$C-5CDD, $^{13}$C-6CDD and $^{13}$C-7CDD to allow calculation of extraction recoveries. The samples were extracted at the following times: 0-weeks, 6-weeks, 12-weeks and 24-weeks. Consistent recovery of the $^{13}$C-4CDD at both high and low levels was obtained; however, at high spike levels of $^{13}$C-8CDD there was a decrease in percentage recovery with an increase in storage time. Inconsistent recoveries were obtained for the $^{13}$C-8CDD at low spike levels due to the fact that the amount spiked was close to the detection limit. This could account for the intermittent detection of the 8CDD in the precipitation samples. A future wall loss study has been initiated and results will be published elsewhere.

The presence of higher congener CDDs and CDFs in three sets of precipitation collection results from an isolated Ontario location indicates that long range transportation and deposition of airborne CDD/CDF does occur. This could account for the low background levels of 8CDD and 8CDF that are found in areas far removed from sites where dioxins are known to exist.

Future research involves the collection of precipitation samples in urban areas to determine the levels of CDD/CDF that are being deposited near industrial areas.

References

1. J.M. Czuczwa and R.A. Hites; Environ. Sci.Technol., 18(1982)444-450.

2. J.M. Czuczwa, B.D. McVeety and R.A. Hites; Chemosphere, 14(1985) 623-626.

Figure 1 SET UP FOR THE SAMPLING OF ORGANICS IN PRECIPITATION